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(12) UK Patent Application (19) GB (11) 2 157 703 A

(43) Application published 30 Oct 1985

(21) Application No 8510024

(22) Date of filing 18 Apr 1985

(30) Priority data

(31) 8410263 (32) 19 Apr 1984 (33) GB

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(51) INT CL⁴

C08G 18/10 18/48 18/66 // C08J 5/18 C09D 3/72 D06M
15/564

(52) Domestic classification

C3R 32A 32D10 32D11A 32D11C 32D12 32D13 32D16A
32D16B 32D1 32D2 32D6C 32D6H 32D6J 32D6K 32D6L
32D8 32D9B1 32D9BX 32D9C 32E10 32E11 32E12
32E2A 32E2DX 32E2E 32E2Y 32E3A 32E3Y 32E6 32E7C
32E7Y 32E8 32G2X 32G2Y 32H5B2 32H5BY 32H8
32J11 32J12 32J1A 32J1Y 32J2C 32J2D 32J2F 32J2X
32J2Y 32J3A 32J3B 32J3Y 32J7A 32J7Y 32KH 32KL
32S 32T2X C11 C12 C25 C9B L2CX L2X L5D L5X L6D
L6G L6H SP W
U1S 1397 1574 1592 1597 1814 3023 3055 C3R

(56) Documents cited

GB A 2087909

(58) Field of search

C3R

(54) Breathable, non-poromeric polyurethane films

(57) A polyurethane which can be used to form a breathable non-poromeric film, is prepared from an isocyanate-terminated prepolymer and a polyol component containing at least 25% of polyoxyethylene units and a low molecular weight constituent having an active hydrogen functionality of at least two, the prepolymer having been formed by reaction of a polyisocyanate with a low molecular weight component having an active hydrogen functionality of at least two.

Uses: - Fabric coatings, film laminates or unsupported films.

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SPECIFICATION

Breathable, non-poromeric polyurethane films

5 This invention relates to breathable, non-poromeric polyurethane films

Our British Patent Application No. 8037510 (Serial No.2087909) describes breathable, non-porous polyurethane films prepared by reaction of a pre-
10 polymer formed from a low molecular weight difunctional compound and an excess of a diisocyanate with polyethylene glycol. However, such films are sometimes rather stiff and inflexible with a high Young's Modulus and are, therefore, unsuitable
15 for use in connection with some type of clothing.

The present invention has been made from a consideration of this problem.

We have discovered that by modifying the polyol component, that is to say the polyethylene glycol
20 component, so as to reduce the hard/soft segment ratio but in such a way that the overall breathability of the film is not substantially altered the initial Young's Modulus can be lowered and a softer film obtained.

25 According to the invention there is provided a breathable, non-poromeric polyurethane formed from a reaction mixture comprising an isocyanate terminated prepolymer, a polyol component containing at least 25% by weight of polyoxyethylene
30 units based on the total weight of constituents, and a low molecular weight constituent having an active hydrogen functionality of at least two, said prepolymer being formed from the reaction product of a polyisocyanate containing at least two isocyanate
35 groups per molecule with a low molecular weight component having an active hydrogen functionality of at least two.

By the invention the viscosity of the reaction mixture is increased by addition of one or more
40 further low molecular weight constituents having a functionality of at least two, preferably a trifunctional component, and which may be the same or different to the low molecular weight component used to form the prepolymer. This increase in viscosity can
45 be obtained without adversely affecting the mechanical properties and breathability of the film. The product of the reaction of the prepolymer and the polyol component has unreacted isocyanate groups. The further addition of a low molecular weight
50 constituent having functionality of at least two increases the viscosity either by promoting more efficient chain extension or by increasing the degree of chain branching. Some polyurethanes may have a certain degree of chain branching and hence
55 those materials, when produced in accordance with the invention will have an even higher viscosity.

The polyisocyanate used in the invention may be any of those used for forming polyurethanes for example toluene -2,4- and toluene -2,6- (and mix-
60 tures thereof), 1,6-hexamethylene, 1,5-naphthalene, 4,4'-diphenylmethane-, 1,4-cyclohexane-, 1,4-phenylene, m- and p-tetramethylxyl-diisocyanates and mixtures thereof. Preferred, however, are isophorone- and 4,4'-dicyclohexylmethane-
65 diisocyanate. Polymeric diisocyanates containing at

least two isocyanate groups per molecule are also suitable.

The low molecular weight active hydrogen component having an active hydrogen functionality of at
70 least two used to form the prepolymer may be a difunctional compound such as a diamine, dihydrazide, diamide, dithiol, dicarboxylic acid, disulphonic acid or mixtures thereof. Preferred, however, are diols such as thiodiglycol, ethylene glycol, dieth-
75 ylene glycol, and butane -1,4-diol. In addition to difunctional compounds, compounds with an active hydrogen functionality of three or more can be used. Examples of trifunctional compounds include triols such as trimethylolpropane, triamines such as dieth-
80 ylenetriamine, and compounds containing more than one type of functional group which may comprise, but is not restricted to, hydroxyl, amine, thiol, carboxylic acid, sulphonic acid, and imide groups. Mixtures of these compounds may also be
85 used. Preferably, the molecular weight of the low molecular weight component is not more than 200.

The polyol component reacted with the prepolymer must be chosen so that the final polymer contains at least 25%, preferably from 25 to 45% of polyox-
90 yethylene units. The preferred polyoxyethylene-containing compound is polyethylene glycol, preferably of molecular weight greater than 400, more particularly within the range 400-2000, and more preferably within the range of 600-1500. Other
95 oxyethylene containing compounds include block copolymers of ethylene oxide with other 1,2-alkylene oxides, such as propylene oxide, butylene oxide; and copolymers formed by reaction of ethylene oxide with polyhydroxy compounds, polyamines, and polythiols.
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The polyol component may consist in part of substances not containing polyoxyethylene units, such as polyester polyols and polyether polyols. Examples of polyester polyols containing at least
105 two terminal hydroxyl groups are polycaprolactone diols and those derived from polyols and organic di- or poly-carboxylic acids. Typical acids used for preparing polyester polyols include diacids such as oxalic, maleic, succinic, adipic, suberic, sebacic, and the isomeric phthalic acids. Polyols used for prepar-
110 ing polyester polyols include, ethylene glycol, diethylene glycol, butane-1,4-diol, 1,6-hexanediol and mixtures thereof, glycerol, trimethylolpropane, pentaerythritol, sorbitol and sucrose. A preferred polyether polyol is polytetramethylene glycol. The
115 polyoxyethylene-containing compound and other polyols may be added to the prepolymer simultaneously or successively. Preferred, however, is successive addition with the polyoxyethylene con-
120 taining compound added last.

The polyol component may comprise a mixture of polyols of different molecular weight. Preferably, when the polyol component comprises polyethylene glycol, the amount of polyethylene glycol is at least
125 25% and preferably not more than 45% by weight of the reaction mixture.

The low molecular weight constituent having an active hydrogen functionality of at least two may comprise a mixture of different compounds. The low
130 molecular weight constituent can comprise a com-

pound having an active hydrogen functionality of three, for example a triol such as trimethylol propane and can comprise compounds containing more than one type of functional group for example

5 hydroxyl, amine, thiol, carboxylic acid, sulphonic acid and amide groups. In other words the low molecular weight constituent can be the same kind of substance as has been described herein as a low molecular weight component for forming the pre-
10 polymer. However, it is not necessary that the low molecular weight constituent and the low molecular weight component should be the same polyurethane formulation according to the invention.

If the proportions of reagent used in the preparation of the polyurethane are such that it still contains residual isocyanate groups, a low molecular weight component having a functionality of at least two can then be added to bring the isocyanate-active hydrogen ratio to unity and thereby increase the viscosity of the resulting polyurethane. Examples of viscosity modifiers or extenders include difunctional compounds such as diols and diamines and preferably trifunctional compounds such as triols, for example trimethylolpropane.

25 The polyurethanes prepared according to the present invention can be used as fabric coatings, film laminates or unsupported films for packaging or medical purposes. In addition, it is possible to improve the mechanical properties and solvent
30 resistance of the polymers by addition of cross linking agents according to standard polyurethane technology. Typical cross linking agents are triisocyanates and melamine formaldehyde resins.

The following examples are illustrative of the
35 invention:-

Example 1

Diethylene glycol (252.9g) in ethyl acetate (250 cm³) was added slowly during 1.5h to a stirred
40 solution of isophorone diisocyanate (1176.5g), dibutyltin dilaurate. (1.1g), and ethyl acetate (1200 cm³) at 50°C. The mixture was stirred for a further 1h, until the isocyanate content reached a constant level, and a solution of polycaprolactone diol, m.w. 830
45 (1092.8g) in ethyl acetate (1100 cm³) was added over 1.0h and the reaction product heated at reflux temperature for 1.5h. Polyethylene glycol, m.w. 1000 (1190.7g) in ethyl acetate (1200 cm³) was then added
50 over 2.0h and the reaction mixture retained at reflux temperature for a further 1.0h, when a solution of trimethylolpropane (35.51 g) was added over 0.5h. After 1.5h an infra red spectrum of the reaction product showed that little isocyanate remained. The
55 intrinsic viscosity of the resulting polymer, measured in dimethylformamide at 25°C, was 0.60.

Cross-linked films of 25 microns thickness were obtained by casting an intimate mixture of the above reaction product (100 g) and Imprafix TH cross-
60 linking agent (4.6 g) onto siliconised release paper, and drying and curing the polyurethane at 100°C (residence time 0.1 - 0.3h). The resulting film had a breaking load of 10.5 MN/m², elongation 879%, and
intrinsic water vapour permeability of 121 g.mm/m²/24h.

65 A solution of the above reaction product contain-

ing 7% w/w Imprafix TH was coated onto woven, filament nylon fabric (120 g/m²) by the knife-over-roll technique. The coated fabric was then dried and cured at 100°C in two passes through the coating
70 machine oven (total residence time approximately 0.2h). The water vapour permeability of the coated fabric (155 g/m²), as measured by the Gore cup method, was 3182 g/m²/day.

Example 2

A prepolymer was prepared as in example 1 from 4,4'-diisocyanatodicyclohexylmethane, Desmodur W (37.39 g), diethyleneglycol (6.82), dibutyltin dilaurate (0.2 g) and a solvent mixture (45 cm³; 50/50 v/v)
80 of dimethylformamide and toluene. Polycaprolactone diol, m.w. 530 (18.90 g) in the mixed solvent (20 cm³) was then added dropwise during 0.4h to the prepolymer solution maintained at 70°C. After 2.0h, polyethylene glycol m.w. 1000 (32.11 g) in the
85 solvent mixture (30 cm³) was added dropwise over 0.5h. After 2.5h, trimethylolpropane (0.95 g) in the mixed solvent (70 cm³) was added and the solution maintained at 80°C for 1.0 h. The intrinsic viscosity of the resulting polymer was 0.67.

90 Films cross-linked with 7% w/w of Imprafix TH had a breaking load of 46.7 MN/m², elongation 578%, and intrinsic water vapour permeability of 71 g. mm/m²/24 h.

Example 3

A prepolymer was prepared as in example 1 from 4,4'-diisocyanatodicyclohexylmethane (527.9 g), diethylene glycol (160.4 g), dibutyltin dilaurate (1.5g), and dimethylformamide/toluene (20/80 v/v;
100 680 cm³). Polyethylene glycol, m.w. 1500 (528.9 g) in the mixed solvent (1100 cm³) was added to the prepolymer solution which was then maintained at 60 - 70° for 2.5 h. Trimethylolpropane (13.5 g) in the
105 mixed solvent (1110 cm³) was finally added and heating continued until an infrared spectrum indicated no residual isocyanate. The intrinsic viscosity of the polymer was 0.91.

Films cross-linked with 7% w/w of Imprafix TH had a breaking load of 37.7 MN/m², elongation 454 %.

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Example 4

A prepolymer was prepared as in example 1 from 4,4'-diisocyanato-dicyclohexylmethane (50.60 g) diethyleneglycol (10.25 g), dibutyltin dilaurate (0.3
115 g), and methyl ethyl ketone (70 cm³). Polycaprolactone diol, m.w. 830 (48.10 g) in methyl ethyl ketone (50 cm³) was added over 0.6 h to the prepolymer solution maintained at 60°C. After 1.5 h Polyethylene glycol, m.w. 1000 (38.62 g) in methyl ethyl ketone (50
120 cm³) was added and heating continued until no isocyanate peak was observed in the infrared spectrum of the reaction product. The intrinsic viscosity of the polymer was 0.27.

Films cross-linked with 10% w/w Imprafix TH had a
125 breaking load of 12.0 MN/m², elongation 678%, and intrinsic water vapour permeability of 102 g. mm/m²/day.

Example 5

130 A prepolymer was prepared as in example 1 from

toluene diisocyanate (80/20 ratio of 2,4- and 2,6-isomers, 29.96g), butane -1,4-diol (7.36g), dibutyltin dilaurate (0.2g) and a solvent mixture (30 cm³; 50/50 v/v) of dimethylformamide and toluene. Polycaprolactone diol, m.w. 993 (38.44g) in the mixed solvent (40 cm³) was then added dropwise over a period of 0.5h, and the solution maintained at 60°C.

Polyethylene glycol m.w. 1000 (38.71g) in the mixed solvent (40 cm³) was added and the solution kept at 60°C for 0.5h. Finally, trimethylolpropane (1.15g) in the mixed solvent (5 cm³) was added and the solution was heated to 80°C for 10h.

The intrinsic viscosity of the resulting polymer was 0.32. Films cross linked with 7% w/w of Imprafix TH had a breaking load of 6.6 MN/M², elongation 300 %, and intrinsic water vapour permeability of 282 g. mm/m²/24hr.

Comparative example

In order to demonstrate that the high water vapour transmission properties of these polyurethanes are specific for the polyethylene oxide structure, a polyurethane was prepared as in example 1, except that the polyethylene glycol m.w. 1000 component was replaced by a molar equivalent of polypropylene glycol m.w. 1025. Thus, a prepolymer was prepared as in example 1 from isophorone diisocyanate (25.61g), diethylene glycol (5.52g), dibutyltin dilaurate (0.1g), and methyl ethyl ketone (28 cm³). Polycaprolactone diol, m.w. 810 (23.29g) in methyl ethyl ketone (35 cm³) was added dropwise to the prepolymer solution maintained at reflux temperature. After 1.5h, polypropylene glycol, m.w. 1025 (26.52g) in methyl ethyl ketone (37 cm³) was added dropwise over 0.5h and the solution kept under reflux for 2h. Trimethylolpropane (0.77g) in MEK (12 cm³) was then added and the reaction mixture maintained under reflux until an infrared spectrum of the product indicated that no isocyanate remained. The intrinsic viscosity of the polymer was 0.62.

Films cross-linked with 7% w/w of Imprafix TH had a breaking load of 9.6 MN/m², elongation 531 %, and intrinsic water vapour permeability of only 17 g. mm/m²/24h.

A carefully deaerated solution of the polypropylene glycol based polyurethane (45% solids in methyl ethyl ketone) containing 7% w/w Imprafix TH was coated onto a woven, filament nylon fabric (20 g/m²) by the knife-over-roll technique. The coated fabric was then dried and cured at 100°C in two passes through the coating machine oven (total residence time 0.2h). The water vapour permeability (Gore cup method) of the coated fabric (156 g/m²) was only 317 g/m²/day.

CLAIMS

1. A breathable non-poromeric polyurethane formed from a reaction mixture comprising an isocyanate terminated prepolymer, a polyol component containing at least 25% by weight of polyoxyethylene units based on the total weight of constituents, and a low molecular weight constituent having an active hydrogen functionality of at least

two, said prepolymer being formed from the reaction product of a polyisocyanate containing at least two isocyanate groups per molecule with a low molecular weight component having an active hydrogen functionality of at least two.

2. A polyurethane as claimed in Claim 1, wherein the low molecular weight component having an active hydrogen functionality of at least two is a polyol, a polyamide or a polyhydrazide.

3. A polyurethane as claimed in Claim 1 or Claim 2, wherein the low molecular weight component having an active hydrogen functionality of at least two contains different functional groups.

4. A polyurethane as claimed in Claim 3, wherein the low molecular weight component having an active hydrogen functionality of at least two contains an hydroxyl, amine, thiol, carboxylic acid, sulphonic acid, or amide group.

5. A polyurethane as claimed in any preceding claim wherein the prepolymer is formed from two or more low molecular weight components having an active hydrogen functionality of at least two.

6. A polyurethane as claimed in any preceding claim wherein two or more low molecular weight constituents having an active hydrogen functionality of at least two are reacted with the prepolymer.

7. A polyurethane as claimed in any preceding claim, wherein the polyol component comprises two or more polyols of different molecular weight.

8. A polyurethane as claimed in any preceding claim, wherein the polyol component comprises at least 25% by weight of polyethylene glycol based on the total weight of the reaction mixture.

9. A polyurethane as claimed in Claim 8, wherein the polyethylene glycol comprises two or more polyethylene glycols of different molecular weight.

10. A polyurethane as claimed in any of Claims 7 to 9 wherein the polyol comprises not more than 45% by weight of polyethylene glycol based on the weight of the reaction mixture.

11. A polyurethane as claimed in any of Claims 7 to 10, wherein the polyol comprises a mixture of polyethylene glycol and an hydroxyl terminated polyester.

12. A polyurethane as claimed in Claim 11, wherein the hydroxyl terminated polyester is a polycaprolactone diol having a molecular weight of from 500 to 2000.

13. A polyurethane as claimed in any preceding claim, wherein the low molecular weight constituent having an active hydrogen functionality of at least two is a triol.

14. A polyurethane as claimed in Claim 13, wherein the triol is trimethylol propane.

15. A polyurethane as claimed in any preceding claim, wherein the low molecular weight constituent having an active hydrogen functionality of at least two contains different functional groups.

16. A polyurethane as claimed in Claim 15, wherein the low molecular weight constituent having an active hydrogen functionality of at least two contains an hydroxyl, amine, thiol, carboxylic acid, sulphonic acid or amide group.

17. A polyurethane as claimed in any preceding claim, wherein the polyurethane is cross-linked.

18. A polyurethane as claimed in Claim 17, wherein cross linking is effected by addition of a cross linking agent to a solution of the polyurethane.

19. A polyurethane as claimed in Claim 18, wherein the cross linking agent is a triisocyanate.

20. A polyurethane as claimed in Claim 18, wherein the cross linking agent is a melamine formaldehyde resin.

21. A breathable, non-poromeric polyurethane substantially as described herein with reference to any one of the Examples.

22. A breathable film prepared by casting a solution of a polyurethane as claimed in any preceding claim and allowing the solvent to evaporate.

23. A fabric coated with a polyurethane as claimed in any of Claims 1 to 21.

Printed in the UK for HMSO, D8818935, 9/85, 7102.
Published by The Patent Office, 25 Southampton Buildings, London,
WC2A 1AY, from which copies may be obtained.

